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# Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene

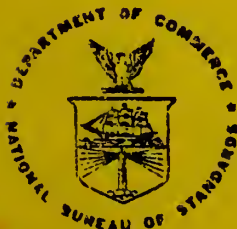
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Third Annual Report for the Period  
October 1, 1981 - September 30, 1982

Task 80-01, NBS-Bureau of Medical Devices Interagency Agreement

March 1983

Issued May 1983



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NATIONAL BUREAU OF STANDARDS

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NBSIR 83-2696 (FDA)

**RELATIONSHIP BETWEEN MORPHOLOGY  
AND MECHANICAL PROPERTIES OF  
ULTRA HIGH MOLECULAR WEIGHT  
POLYETHYLENE**

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J. M. Crissman  
Principal Investigator

L. J. Zapas  
Project Leader

F. A. Khoury  
Project Leader

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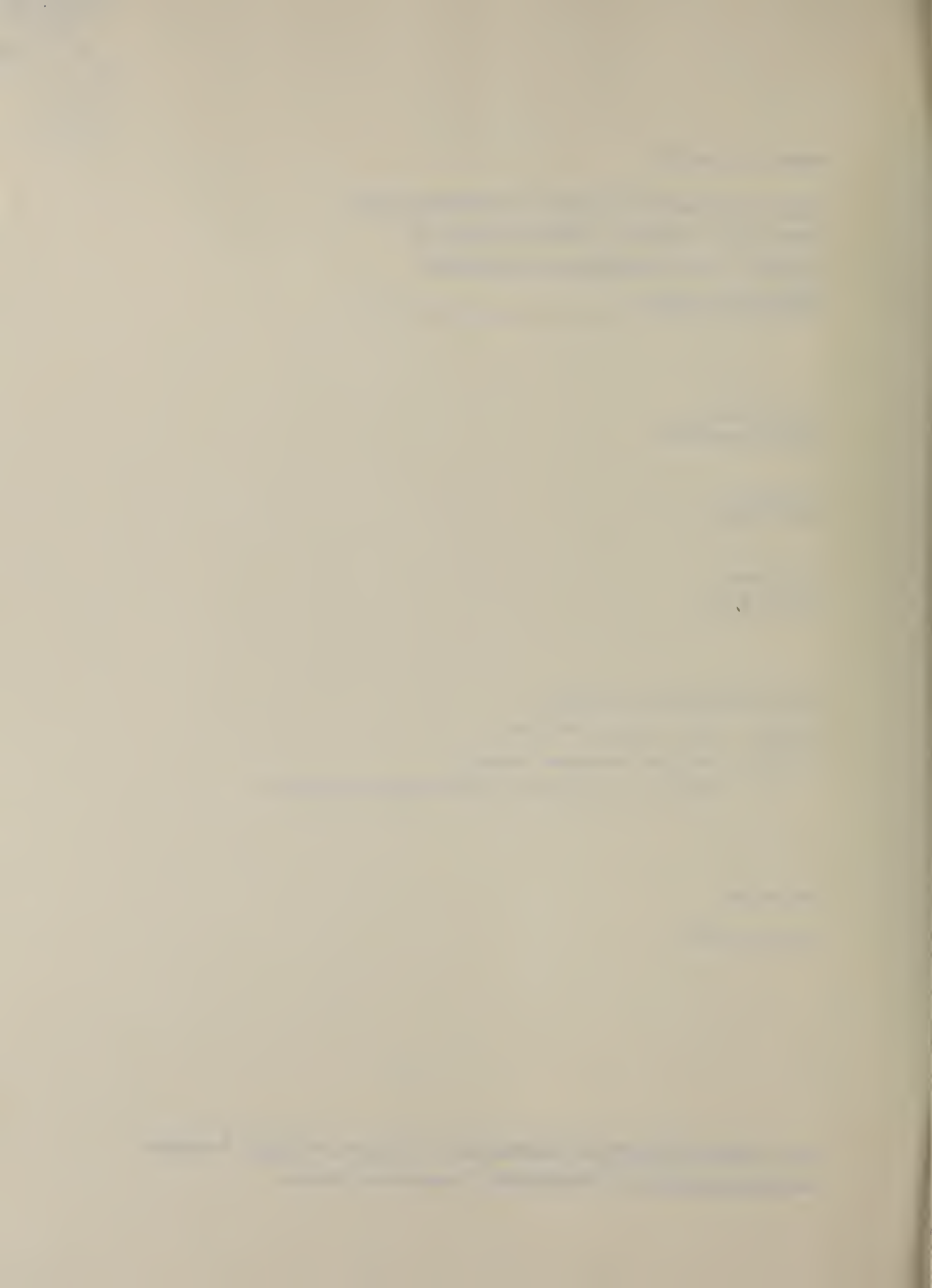
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**U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary***  
**NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director***



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### Abstract

This report describes work done during FY 1982 under task 80-01, NBS-FDA/BMD (Bureau of Medical Devices) Interagency agreement. The report covers the third year of a four year project concerned with the study of the morphology and mechanical properties of ultra high molecular weight polyethylene (UHMWPE). During FY 1982, the two principle areas of investigation were (1) the examination by x-ray diffraction of morphological changes occurring in UHMWPE while under strain, and (2) the creep and recovery behavior of UHMWPE at small deformations. A new one dimensional constitutive equation is presented which describes very well the creep and recovery behavior of this material at small deformations.



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## 1. Introduction

This report describes work done during FY 1982 under task 80-01, NBS-BMD (Bureau of Medical Devices) Interagency Agreement. Background information relevant to this work, as well as a summary of the work done during FY 1980 and FY 1981, can be found in references [1] and [2]<sup>†</sup>.

During FY 1982, the two principal areas of investigation were

(1) the examination by x-ray diffraction of morphological changes occurring in UHMWPE while under strain, and (2) the creep and recovery behavior of UHMWPE at small deformations. A comparison of the creep and recovery behavior of specimens prepared under different thermal histories is also presented.

## 2. Structural Changes Associated with the Uniaxial Stretching of Ultra High Molecular Weight Polyethylene (UHMWPE).

### 2.1 Background

As indicated in previous reports [1,2] compression molded samples of the UH-A and UH-C ultra high molecular weight polyethylenes do not exhibit macroscopic necking when stretched uniaxially. Furthermore they undergo large recoveries from deformation (even from large strains) when they are released under zero stress. For example, samples which were stretched to a strain of 3.0 at a rate of 0.02/min exhibited residual strains in the range 172% - 192% twenty four hours after they were released (see Table 6, ref.[2]).

Our previous studies of the structure and orientation changes resulting from uniaxial stretching at room temperature and at 37°C have been limited to an examination of the wide angle [1,2] and small angle [1] x-ray diffraction patterns exhibited by the stretched samples after they had been allowed to contract under zero tension for periods in excess of twenty four hours. The residual strains in the

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<sup>†</sup> Numbers in brackets indicate references found at the end of this report.

released samples were of course larger the higher the initially imposed strain, and ranged from 0.2 to 3.0. Among the features which were observed in all these samples [1,2] was the presence of a small proportion of crystallites exhibiting wide angle x-ray reflections characteristic of the metastable crystalline form of polyethylene [3,4]. The structure of the remaining majority of the crystallites was the normal orthorhombic structure [5].

The metastable crystalline form of polyethylene usually occurs in small proportions and is quite common in variously deformed lower molecular weight polyethylene samples. It is characterized in particular by three wide angle x-ray reflections corresponding to interplanar spacings of  $0.45_5\text{nm}$ ,  $0.38_0\text{nm}$ , and  $0.35_5\text{nm}$ . These spacings differ significantly from those of the prominent orthorhombic 110 and 200 reflections which are  $0.41\text{nm}$  and  $0.37\text{nm}$  respectively.

Two different but related unit cells have been proposed for the metastable crystalline form of polyethylene. The cell proposed by Turner-Jones [3] is triclinic with  $a=0.4285\text{nm}$ ,  $b=0.4820\text{nm}$ ,  $c=0.254\text{nm}$ ,  $\alpha=90^\circ$ ,  $\beta=110.25^\circ$ ,  $\gamma=108^\circ$ , whereas that proposed by Seto, Hara, and Tanaka [4] is monoclinic with  $a=0.809\text{nm}$ ,  $b=0.253\text{nm}$ ,  $c=0.479\text{nm}$  and  $\beta=107.9^\circ$ . The indices of the  $0.45_5$ ,  $0.38_0$ , and  $0.35_5$  reflections based on the triclinic cell [3] are 010, 100 and  $1\bar{1}0$  respectively. The corresponding indices based on the monoclinic cell [4] are 001, 200 and  $\bar{2}01$ . As we have done previously in our discussions of the wide angle x-ray diffraction patterns exhibited by strained samples after they were allowed to contract, we shall identify the three above mentioned reflections associated with the

metastable crystalline form of polyethylene in terms of their indices based on the triclinic cell [3]. A subscript t will be appended to the indices of the reflections to distinguish them from the orthorhombic reflections.

The exploratory experiments described below represent additional steps in an effort aimed at determining the structural changes associated with the deformation, and the partial recovery from deformation, of compression molded UHMWPE.

## 2.2 Structural Changes in Samples Stretched and Held at Strains in the Range of 0.1 to 1.0.

Evidently, determination of the nature of the processes which underlie the partially reversible deformation behavior exhibited by compression molded UHMWPE requires knowledge of the structure of the strained samples before and after they are released. The experiments described below represent a first step in establishing a basis for comparing our earlier observations on the structures of stretched samples after they are released, with the structures exhibited by the samples prior to being released.

The wide angle x-ray diffraction (WAXD) patterns shown in Fig.1 were all obtained from the same dumbbell shaped sample of compression molded UH-C polymer. The density of the sample was  $0.941 \text{ g/cm}^3$ . The pattern in Fig.1a represents the unstretched sample. This sample was stretched to progressively larger strains in a stepwise manner up to a strain of 1.0. Stretching was carried out in a simple hand operated stretching frame. After each of seven increases in clamp separation the corresponding strain in the gauge section of the specimen was determined, following which a WAXD pattern was recorded

photographically using a flat plate camera and Ni filtered  $\text{CuK}_\alpha$  x-ray radiation [Figs. 1, b-h]. At least ten minutes were allowed to lapse after each increase in imposed strain before the corresponding pattern was recorded using an exposure time of ten minutes. The sample was held taut throughout these experiments.

The following features and trends exhibited in Figs. (1,a-h) may be noted:

(i) As pointed out in previous reports the WAXD pattern of the unstretched specimen (Fig.1a) exhibits a very diffuse inner ring (H), which is attributable to the amorphous regions in the sample, as well as the two intense 110 and 200 diffraction rings characteristic of orthorhombic polyethylene.

(ii) At strains of 0.1 to 1.0 (Figs.1, b-h) the stretched sample exhibits the normal orthorhombic reflections, as well as the 'extra' reflections characteristic of the metastable crystalline form of polyethylene. The intrinsically most intense among the latter reflections, namely the  $101_t$ , can be readily seen even at a strain of 0.1. The weaker  $100_t$  and  $\bar{1}10_t$  which are barely visible at low strains tend to become all the more evident the higher the strain indicating that the proportion of metastable triclinic crystallites increases with increasing strain.

(iii) As can be seen in Figs. 1 (b-c) the azimuthally broad (arced)  $010_t$  reflections centered on the meridian (which corresponds to the stretching direction) and the much less intense  $\bar{1}\bar{1}0_t$  arcs centered on the equator are characteristic features of the WAXD patterns obtained at small strains in the range 0.1-0.2. At higher



strains, the  $1\bar{1}0_t$  arcs remain centered on the equator indicating that among the planes which are parallel to the c-axis (and hence the chain axis direction) in the triclinic crystallites, the  $(1\bar{1}0)_t$  planes are the first to become oriented preferentially parallel to the stretching direction. The  $010_t$  arcs seen in Figs.1(b-c) split progressively at higher strains (Fig. d-h) into two broad arcs. The azimuthal angle  $\psi_{010t}$  between the most intense portions of these arcs and the stretching direction increases with increasing strain. At a strain of 1.0,  $\psi_{010t}$  is about  $60^\circ$  and  $\psi_{100t}$  is  $\approx 65^\circ$ . On the basis of these azimuthal dispositions of the  $010_t$  and  $100_t$  arcs, as well as the preferential equatorial disposition of the  $1\bar{1}0_t$  arcs, it can be estimated (see e.g. Ref.6) that whereas the triclinic crystallites are oriented with the  $(1\bar{1}0)_t$  planes preferentially parallel to the stretching direction, the distribution in the angle of inclination of the c-axis (and hence the chains) in the crystallites relative to the stretching direction is peaked at about an angle of  $\approx 30^\circ$ .

(iv) The effect of increasing strain on the orientation of the orthorhombic crystallites is qualitatively similar to the trends exhibited in the lower molecular weight polyethylenes [6,7], as well as those observed in our earlier examination of samples of UHMWPE which had been allowed to contract freely after being stretched to various strains [1,2]. Typically the (200) planes are the first to orient themselves preferentially parallel to the stretching direction. The manifestation of this feature is evidenced at small strains by the progressive increase in the intensity of the 200 diffraction ring in the equatorial region relative to that in the meridional region (Fig.1, b-d). At higher strains (e.g.  $>0.3$ , Figs.1, e-h) the 200

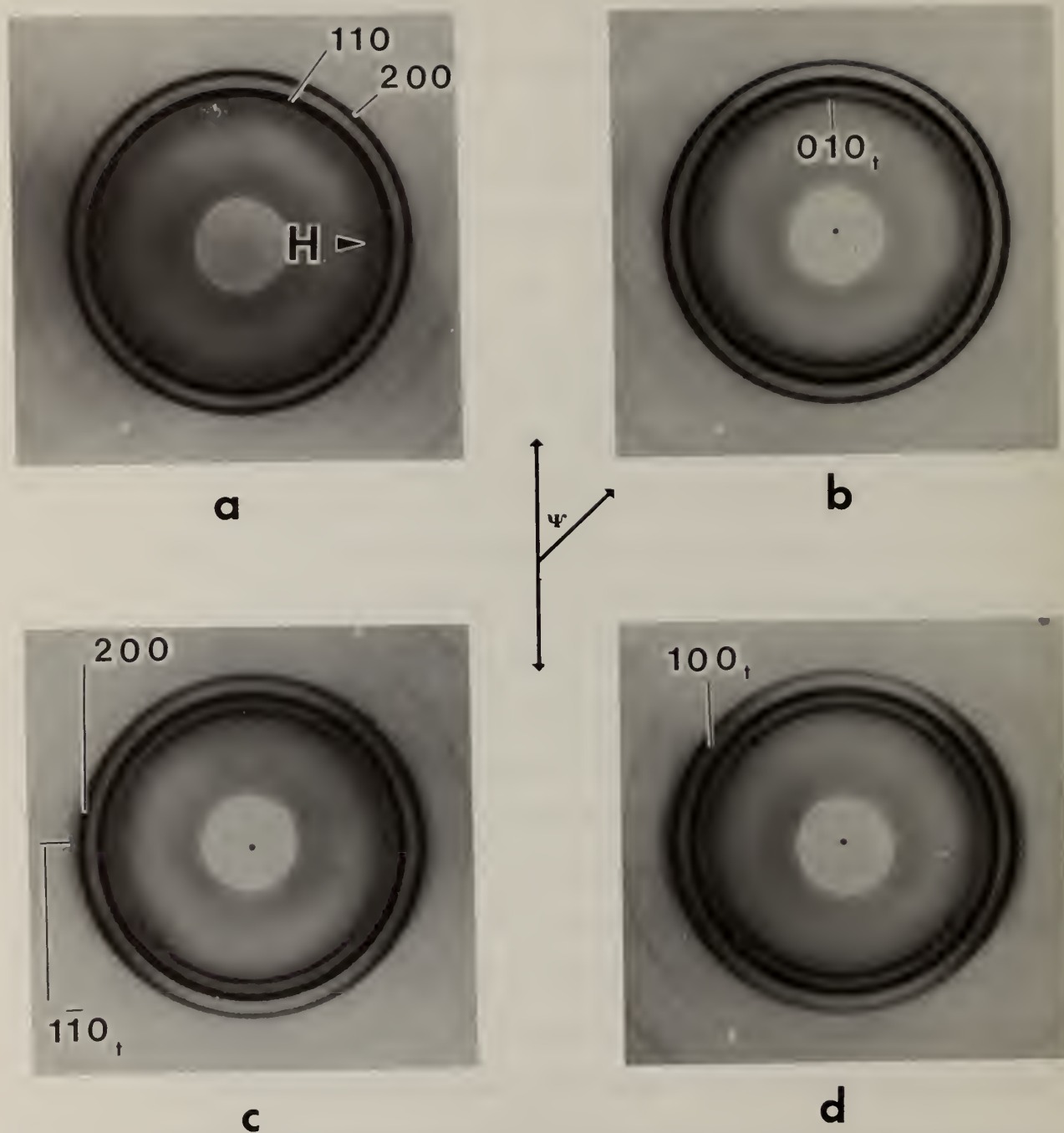


Figure 1 Wide angle x-ray diffraction patterns. (a) Unstretched compression molded sample of UH-C; H denotes amorphous ring. (b-h) Same sample after it was stretched and kept taut at strains of (b) 0.1, (c) 0.15, (d) 0.23, (e) 0.3, (f) 0.48, (g) 0.64 and (h) 1.0. Stretching direction vertical.  $\psi$  is azimuthal angle.

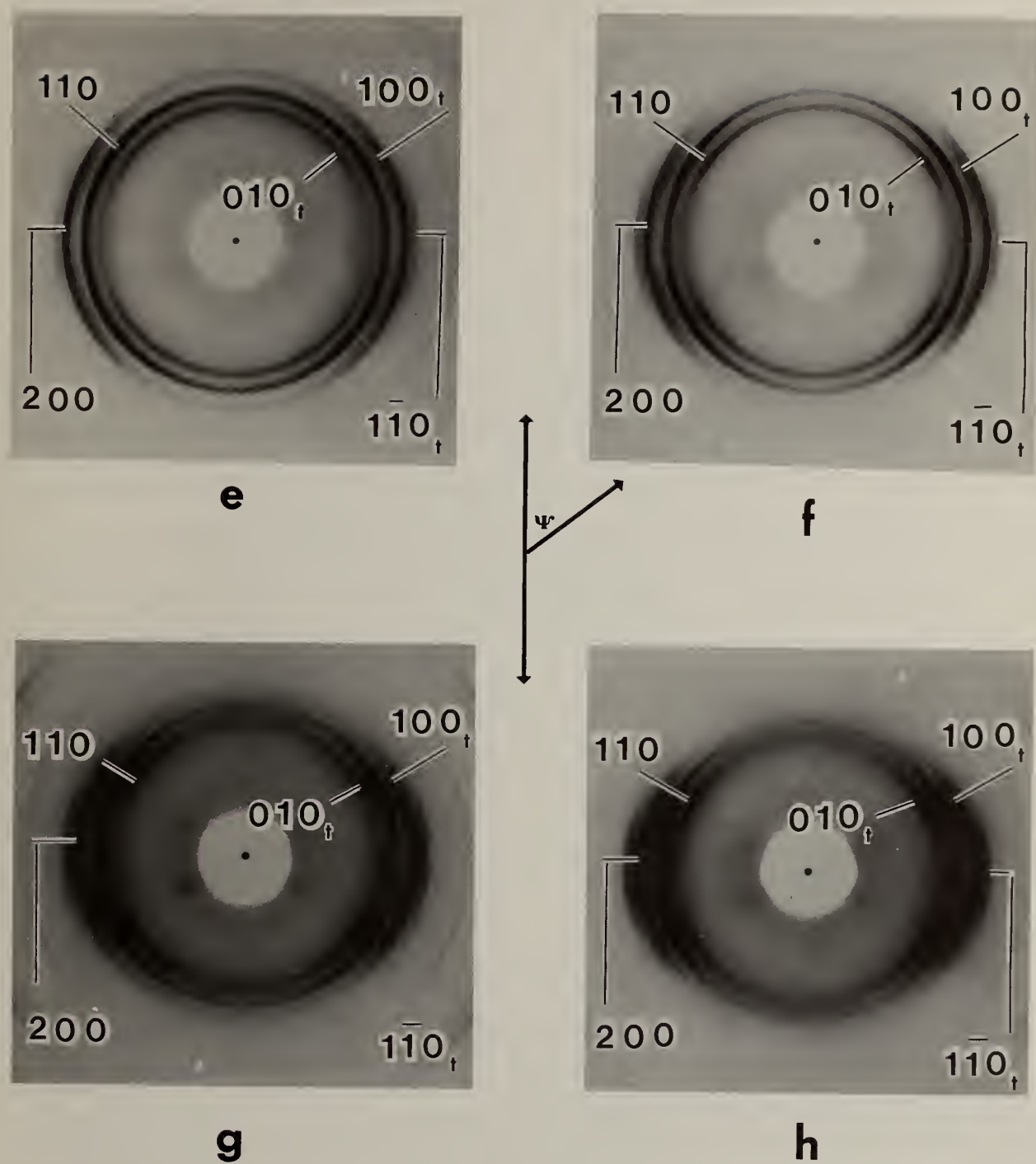


Figure 1 (contd)



reflections occur as arcs centered on the equator. The orientation of the (110) planes with increasing strain is characterized by the progressive splitting of the 110 diffraction ring into two pairs of broad arcs. The azimuthal angle  $\psi_{110}$  between the most intense portion of these arcs and the stretching direction increases progressively with increasing strain, and, correspondingly, the overlap between the arcs increases in the equatorial region. This trend reflects the increasing tendency for the orthorhombic crystallites to orient themselves with the c-axis (and hence the chains) more closely parallel to the stretching direction with increasing strain. At a strain of 1.0  $\psi_{110} \approx 60^\circ$ . Using this value for  $\psi_{110}$  and the equatorial orientation of the 200 reflections as a basis, it may be estimated that the distribution in the angle of inclination of the c-axis (and hence the chains) of the orthorhombic crystallites relative to the stretching direction is peaked about an angle of  $\approx 36^\circ$ .

In summary, the following qualitative features emerge from the experiment described above concerning the effect of strain on the manifestation of polymorphism and the changes in crystallite orientation resulting from uniaxial stretching:

- (a) The occurrence of metastable (triclinic) crystallites manifests itself at all strains in the range 0.1 to 1.0. The proportion of triclinic crystallites apparently increases with increasing strain in that range.
- (b) The triclinic and orthorhombic crystallites start to align themselves respectively with the  $(010)_t$  planes and the (200) planes preferentially parallel to the stretching direction from the early stages in deformation.
- (c) The distributions in the angle of inclination of the c-axis in the triclinic and orthorhombic crystallites relative to the stretching direction at a strain of 1.0 are peaked at inclinations of roughly  $30^\circ$  and  $36^\circ$  respectively.

The sample used in the experiment described above was released under zero stress. The WAXD pattern shown in Fig.2 was taken after it had contracted from an initial strain of 1.0 to a strain of 0.4. It is evident from a comparison of Fig. 2 with Fig. 1h (strain 0.1, sample taught) that one of the main changes which occurred when the sample contracted was a substantial decrease in the proportion of triclinic crystallites. Thus, in contrast with Fig.1h, the  $1\bar{1}0_t$  and  $100_t$  reflections are barely if at all visible in Fig.2. Furthermore the intensity of the  $010_t$  arcs relative to  $110$  orthorhombic arcs appears to be considerably diminished in Fig.2 as compared to Fig.1h. Indeed, comparison of Fig.2 with the WAXD patterns of the stretched-unreleased sample at comparable strains, i.e. Fig.1e (strain 0.3) and Fig.1f (strain 0.475), indicates that the proportion of triclinic crystallites is higher in the latter two cases than in the released sample.

The exploratory experiments described above clearly indicate that the characterization of the partially reversible deformation behavior of UHMWPE must involve not only the quantitative determination of the changes in crystallite orientation in the samples, but also quantitative determination of the relative amounts of the different crystalline forms.

With regard to the recent interest (see Section 3) in the behavior of UHMWPE under the influence of low stresses (and hence small strains), we have examined the WAXD patterns exhibited by samples stretched up to a strain of 0.05 in an attempt to determine the lower limit of deformation at which the occurrence of triclinic crystallites manifests itself. This limit remains to be explored quantitatively using densitometry to examine the diffraction patterns. One complication which should be noted is that the



Figure 2 Same sample as Fig. 1 after it was released and had contracted from a strain of 1.0 (Fig.1(h)) to a strain of 0.4. Original stretching direction vertical.

intrinsically most intense of the triclinic reflections, i.e. the  $010_t$ , corresponds closely with that of the amorphous halo (H) in the samples.

However, the occurrence of weak and azimuthally broad meridional  $010_t$  arcs was visually evident in the diffraction patterns of samples stretched and kept taut at a strain of 0.05.

### 3. Mechanical Behavior Studies

In reference [2] a set of experiments was described in which cylinders of UHMWPE were subjected to creep in compression at a constant applied load followed by recovery at zero load. The recovery data were presented in Figure 15 of reference [2]. Also shown in the same figure was the strain during recovery predicted assuming a superposition principle [3] of the form

$$\epsilon_R(t) = \epsilon_c(t + t_1) - \epsilon_c(t) \quad (1)$$

where  $\epsilon_R(t)$  is the strain during recovery at a time  $t$  after a creep experiment of duration  $t_1$ , and  $\epsilon_c(t + t_1)$  and  $\epsilon_c(t)$  are the strain in a creep experiment at time  $t+t_1$  and  $t$ . In the experiments described in reference [2] the duration of both the creep step and the recovery step was fixed at 3300 seconds and the magnitude of the applied stress was varied. It was found that the recovery at the early times agreed well with the predicted values, but at the longer recovery times approaching  $t_1$  the actual recovery was significantly less than was the predicted recovery.

Since the ability of UHMWPE to recover after deformation represents an important aspect of durability and lifetime, we have examined in some detail the creep and recovery behavior of UHMWPE at small deformations for widely different creep histories and preparation conditions. In sections 3.1 and 3.2 we shall describe two step and multistep creep and recovery experiments done on the material designated as slowly cooled UH-A in reference [2]. The results of these experiments led us to formulate a new



one dimensional constitutive equation which describes plasto-viscoelastic behavior. In the new derivation the assumption is made that the undeformed state of the material depends upon the prior stress history. In Section 3.3 the creep and recovery behavior of the slowly cooled UH-A will then be compared to that of quenched UH-A and annealed UH-A.

### 3.1 Two Step Creep and Recovery

The present experiments were done in uniaxial extension rather than in uniaxial compression which was the case in reference [2]. Provided that the maximum creep strains are sufficiently small, the creep experiment can be considered a constant true stress experiment. It is anticipated that in this range of deformations the behavior in extension will not be significantly different from that in compression. Moreover, it is possible to cut several tensile bars from each sheet of material thereby minimizing specimen to specimen variability, whereas each cylinder must be prepared individually.

In a two step creep and recovery experiment the specimen is subjected to a constant applied stress,  $\sigma_A$ , for a time  $t_1$ , after which the applied stress is removed and the specimen is maintained at zero load thereafter. The specimen strain is determined as a function of time during both the creep and recovery portion of the experiment. For each experiment a fresh specimen was used (no prior deformation history) and care was taken in handling the specimen prior to and during mounting of the specimen in the test machine.

The first set of experiments to be described involves creep for  $10^3$  seconds followed by recovery for times of up to  $10^4$  seconds. The data are presented in Figure 3 for experiments carried out at applied stresses in the range from 1 to 8 MPa. This range of applied stresses

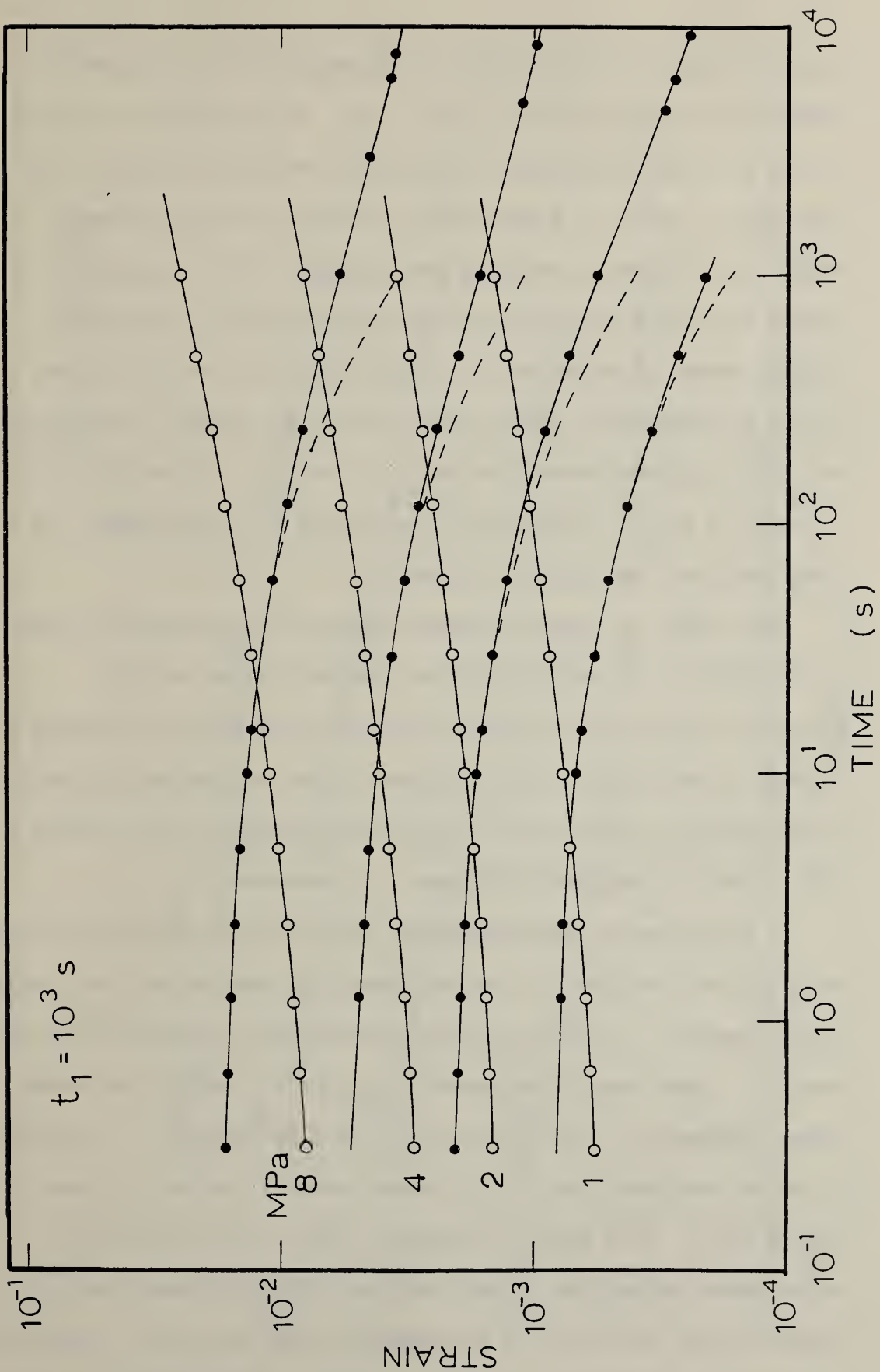


Figure 3 Creep strain (O-O) and strain during recovery (●-●) versus time (log-log coordinates) from experiments carried out at constant  $t_1$  but varied applied stress  $\sigma_A$ . The dashed lines represent the recovery predicted using equation 1.

includes those which are likely to be experienced by the UHMWPE component of a prosthesis in actual use. We note that an applied stress of 1 MPa corresponds to a load of less than 1 kg (for our specimens). Thus it is important in setting up the experiment that care is taken in handling the specimens. By inspection of Figure 3 it can be seen that at an applied stress of 8 MPa the maximum strain attained at  $10^3$  seconds was 0.025, whereas at  $t=1$  second the strain was about 0.009, so that the applied stress during the creep step was constant within 1.5 percent. For smaller values of  $t_1$ , even up to  $t_1 = 10^2$  seconds, the change in stress during the creep step was less than 0.5 percent.

Also shown in Figure 3 (dashed lines) is the behavior predicted by equation 1. At early times the observed values and the predicted values of the recovery coincide, whereas at the longer recovery times approaching  $t_1$  the two curves deviate significantly. This behavior is equivalent to that noted earlier for the slowly cooled UH-C in compression (Figure 15, reference [2]).

A second set of experiments was done in which the applied stress was held constant and the time of creep,  $t_1$ , was varied from 1 second to  $10^3$  seconds. In each case the recovery was monitored for up to  $10^4$  seconds. These results are shown in Figure 4. Again, the dashed lines correspond to the recovery predicted by equation 1. In Figure 4 it can be seen that the strain during recovery tends to plateau to a finite value. This behavior has been found to be true also for experiments carried out at much smaller applied stresses where the maximum creep strain was of the order of 0.001 and less. This behavior cannot be described by the various non-linear viscoelastic theories of simple materials.



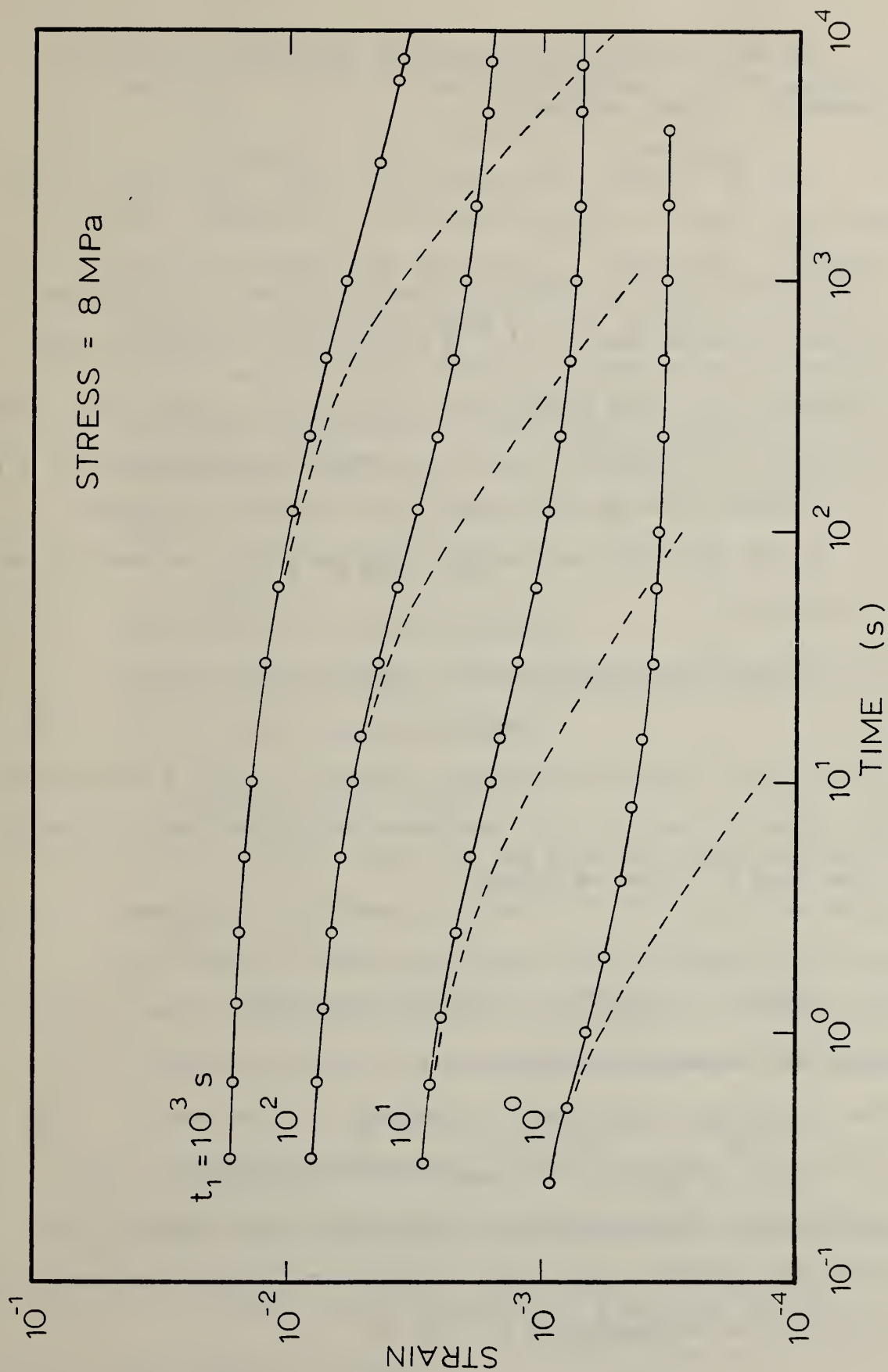


Figure 4 Strain during recovery (log-log coordinates) from experiments done at constant applied stress but varied  $t_1$ . The dashed lines represent the recovery predicted using equation 1.

We now introduce the following one dimensional constitutive equation. At small deformations,

$$\varepsilon(t) = \int_0^t J_*(\sigma(\xi), t-\xi) d\xi + J(\sigma(t), 0) + \phi \left( \int_0^t \hat{g}(\sigma(\xi)) d\xi \right). \quad (2)$$

In equation 2,  $\varepsilon(t)$  is the strain observed at time  $t$ ,  $\sigma(\xi)$  is the applied stress at time  $\xi$ ,  $\phi \left( \int_0^t \hat{g}(\sigma(\xi)) d\xi \right)$  is a functional which depends on the stress history, and  $J(\sigma, t)$  is in the manner of a non-linear compliance multiplied by  $\sigma$ .  $J_*(\cdot, \cdot)$  denotes the derivative of  $J(\cdot, \cdot)$  with respect to the second argument, and  $J(0, t) = J_*(0, t) = \hat{g}(0) = 0$ .

For the two step creep and recovery experiment just described, it can be shown that

$$\begin{aligned} \varepsilon_R(t_1; t) = \varepsilon_c(\sigma; t+t_1) - \varepsilon_c(\sigma; t) - \phi(\hat{g}(\sigma)(t+t_1)) + \phi(\hat{g}(\sigma)t) \\ + \phi(\hat{g}(\sigma)t_1), \end{aligned} \quad (3)$$

where  $\varepsilon_R(t_1; t)$  is the strain during recovery at a time  $t$  after creep for a time  $t_1$ , and  $\varepsilon_c(\sigma; t)$  is the strain during the creep at a stress  $\sigma$  and time  $t$ . If we now define,

$$\varepsilon_R(t_1; t) - \varepsilon_c(\sigma; t+t_1) + \varepsilon_c(\sigma; t) = \Delta\varepsilon_{RC}(t_1; t), \quad (4)$$

then for the case where  $t=t_1$ ,

$$\Delta\varepsilon_{RC}(t_1; t_1) = 2\phi(\hat{g}(\sigma)t_1) - \phi(\hat{g}(\sigma)2t_1). \quad (5)$$

In equation 5  $\Delta\varepsilon_{RC}(t_1; t_1)$  represents the deviation of the actual recovery from that calculated using equation 1 (at a time  $t_1$  after creep for a duration  $t_1$ ). If it is now assumed that in its simplest form  $\phi(\hat{g}(\sigma)t_1)$  can be represented by

$$\phi(\hat{g}(\sigma)t_1) = g(\sigma)t_1^\alpha, \quad (6)$$

where  $g(\sigma) = (\hat{g}(\sigma))^\alpha$ , then from equation 5 it follows that

$$\Delta\epsilon_{RC}(t_1; t_1) = g(\sigma)(2-2^{1/3}) t_1^\alpha = (\text{constant}) t_1^\alpha. \quad (7)$$

For constant  $\sigma$  a plot of  $\log \Delta\epsilon_{RC}(t_1; t_1)$  versus  $\log t_1$  should then yield a straight line with slope  $\alpha$ . Such a plot is shown in Figure 5 for six experiments in which  $t_1$  was varied from 1 second to  $10^3$  seconds. (Four of the curves are shown in Figure 4.) To a very good approximation the data can be represented by a straight line having a slope of one third. Equation 7 can then be rewritten as

$$\Delta\epsilon_{RC}(t_1; t_1) = 0.74 g(\sigma) t_1^{1/3}, \quad (8)$$

from which  $g(\sigma)$  can be determined.

It was also found that the creep curves can be represented rather well by the following relation:

$$\epsilon_c(\sigma; t) = f_1(\sigma) + f_2(\sigma) t^{1/3}. \quad (9)$$

In the case where both the function  $\phi$  and  $J$  have the same exponential dependence on time, as is the case in the present work, it can easily be shown that recovery data, obtained from creep experiments having different durations  $t_1$  (at constant  $\sigma$ ), can be superposed onto a master curve with predetermined shift factors. For example, in the present work the recovery at time  $t$  after a creep for time  $t_1$  is given by

$$\epsilon_R(t_1; t) = \theta(\sigma)[(t+t_1)^{1/3} - t^{1/3}] + g(\sigma) t_1^{1/3}, \quad (10)$$

where  $\theta(\sigma) = f_2(\sigma) - g(\sigma)$ . Then the recovery  $\epsilon_R(\hat{t}; t_i)$ , where  $t_i = \alpha_i t_1$ ,

$$\text{is } \epsilon_R(\hat{t}; t_i) = \theta(\sigma) \left[ (\hat{t} + \alpha_i t_1)^{1/3} - \hat{t}^{1/3} \right] + g(\sigma) \alpha_i^{1/3} t_1^{1/3}. \quad (11)$$

For values of  $\hat{t} = \alpha_i t$ ,

$$\epsilon_R(t_1; t) = \alpha_i^{-1/3} \epsilon_R(\alpha_i t_1; \alpha_i \hat{t}). \quad (12)$$

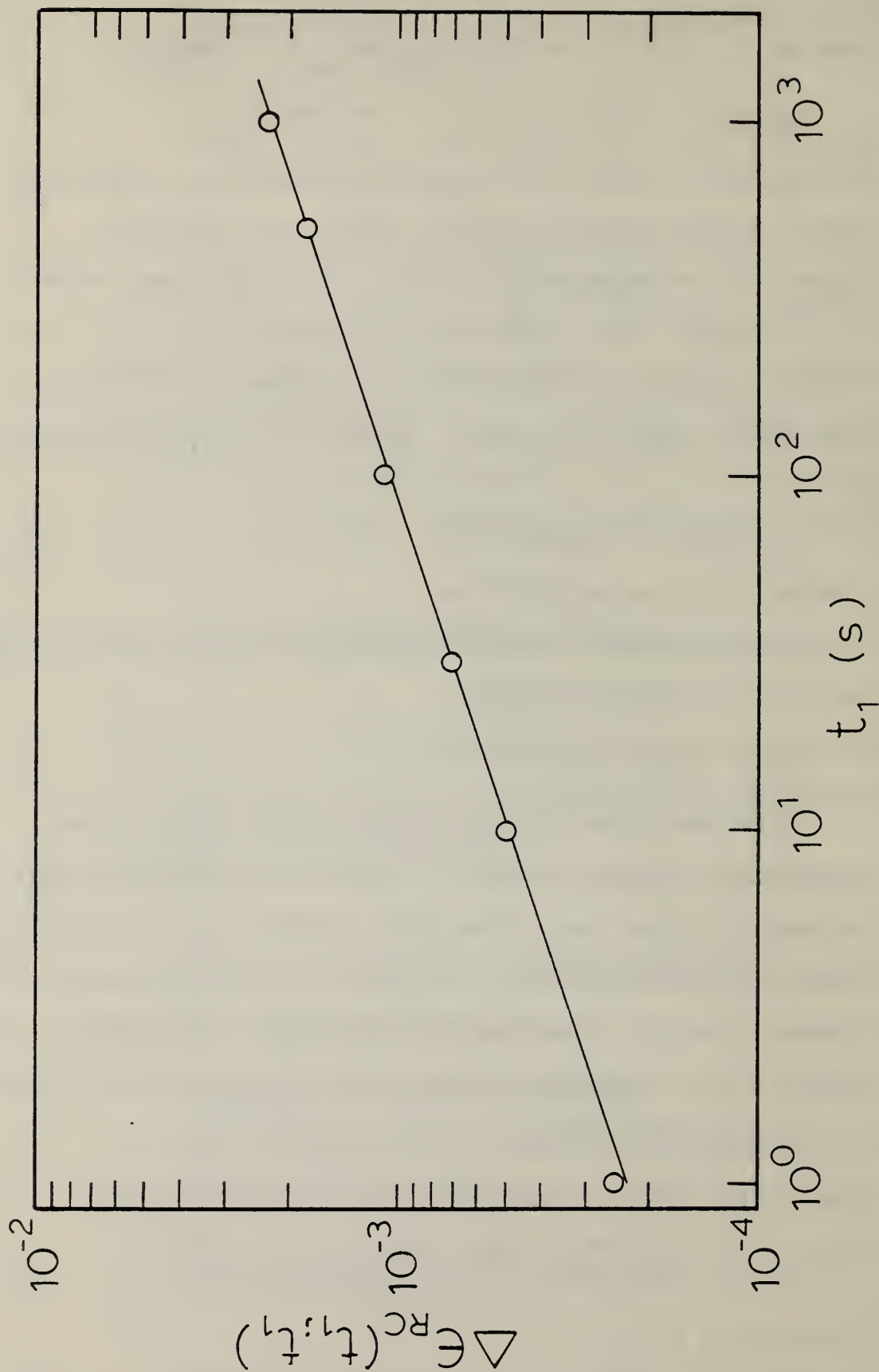


Figure 5 Values of  $\Delta \epsilon_{RC}(t_1; t_1)$  versus  $t_1$  on log-log coordinates.

Starting from an experiment for which the recovery is  $\epsilon_R(t_1, t)$ , we can then superpose any other recovery data  $\epsilon_R(\hat{t}; t_1)$  by first dividing by  $\alpha_i^{1/3}$  (the ratio of  $t_1/t_1$ ), and then shifting along the time axis by  $\alpha_i$ . This procedure was carried out for the data shown in Figure 4, and the results are presented in Figure 6, where  $t_1$  was taken to be  $10^3$ s. From Figure 6 it is evident that the material will stop recovering after a time greater than about  $10^6$ s, or a time three orders of magnitude greater than the step time  $t_1$ .

The functions  $f_1(\sigma)$  and  $f_2(\sigma)$  can be determined from the data shown in Figure 3 where the time  $t_1$  was held constant, but the magnitude of the applied stress was varied from 1 to 8 MPa. By using values of these functions and value of  $g(\sigma)$  determined with equation 8 we were able to reproduce all of the recovery data to within two percent or better. Examples of the calculated values of the recovery are shown in Figure 7, where the solid lines represent the actual data and the open circles the calculated values. It can be seen that there is excellent agreement between the two sets of results.

### 3.2 Multistep in Stress Creep and Recovery Experiments

We have also considered more complicated stress histories involving multistep creep and recovery. In one set of experiments the material, having been at rest up until time  $t=0$ , was subjected to the multistep stress histories indicated in Figures 8 and 9. For these experiments the extensometer was not reset to zero throughout the course of the experiment. The observed responses for the creep and recovery steps are shown in Figures 8 and 9 as sets of curves labelled 1-4. The time at the onset of each step is taken to be the time  $t=0$ . The points (circles and triangles) are the values of the strain calculated using equation 2. The agreement is indeed very good. At the early times the creep strain



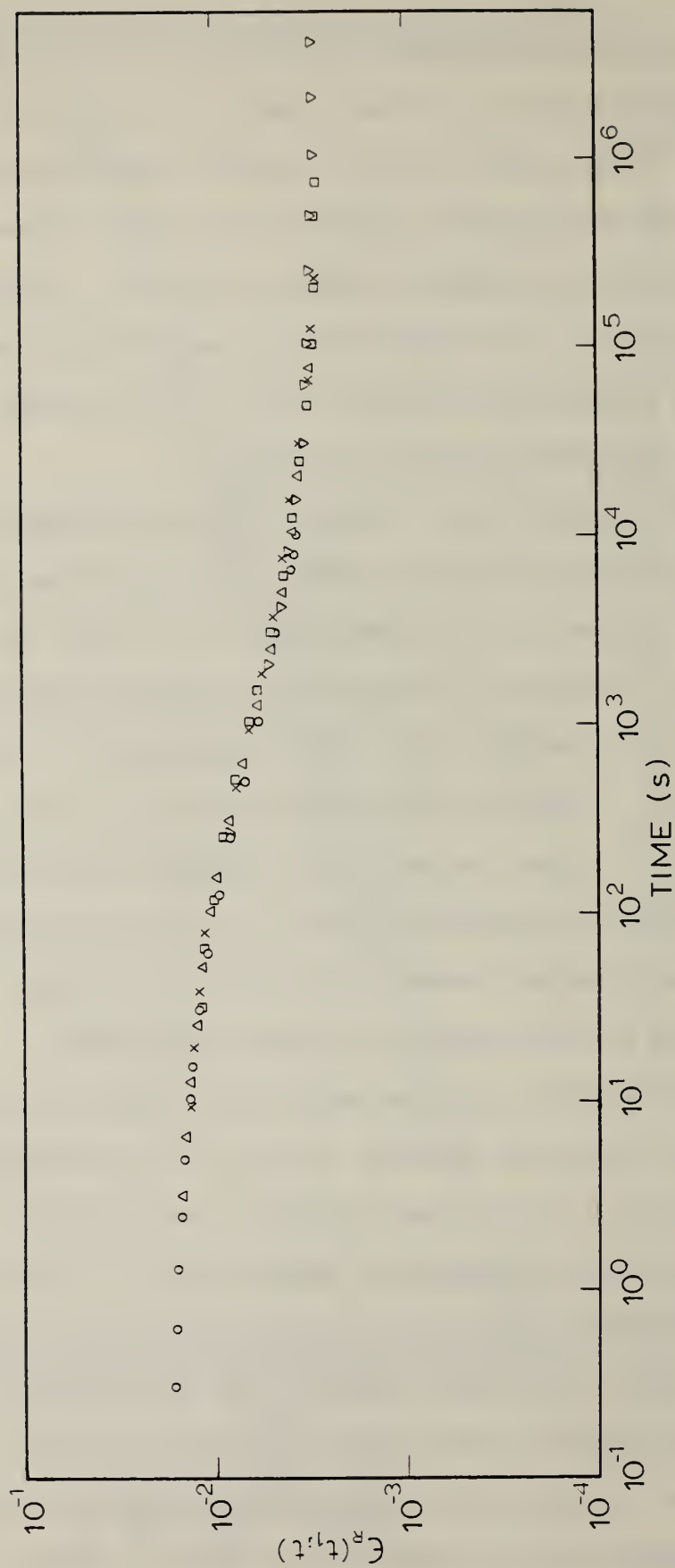


Figure 6 Superposition of the recovery data shown in Figure 4 onto a master curve.

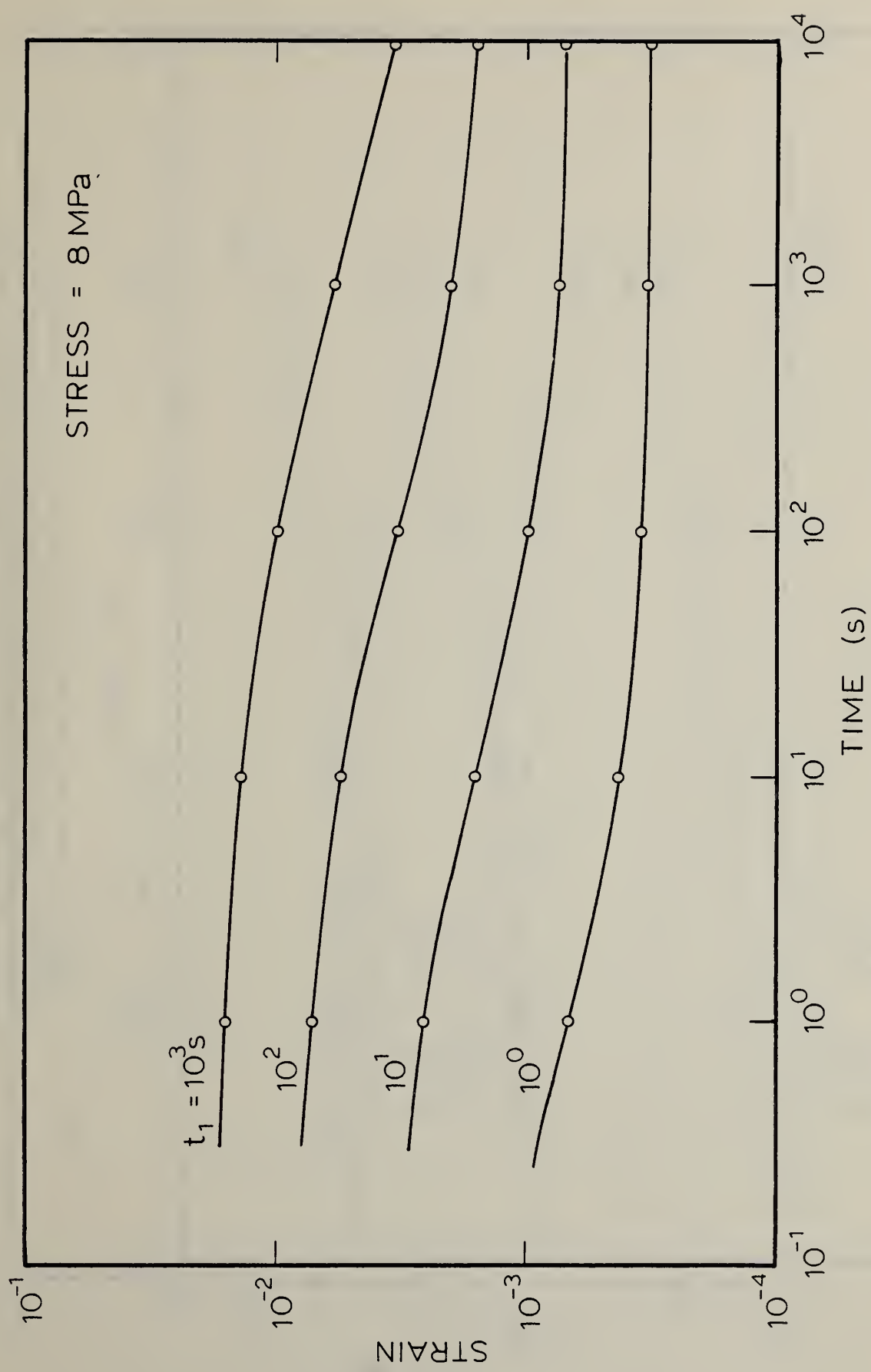


Figure 7 Comparison of the recovery data shown in Figure 3 (solid lines) and the values of recovery (circles) predicted using equation 2.



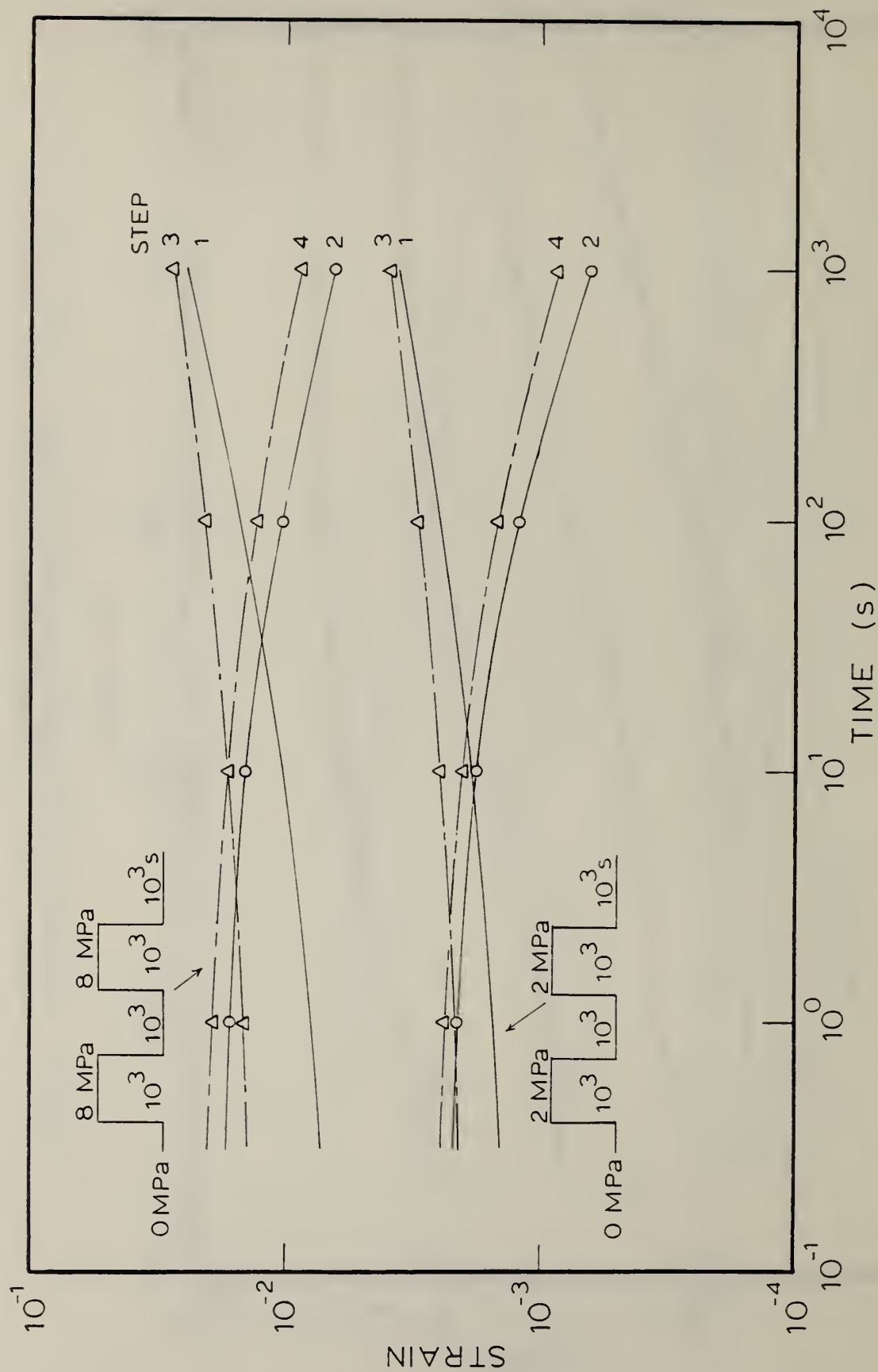


Figure 8 Multistep creep and recovery data for the stress histories indicated. The creep data are represented by the curves labelled 1 and 3, and the recovery data by the curves labelled 2 and 4. The triangles and circles are the predicted values of the creep and recovery calculated using equation 2.

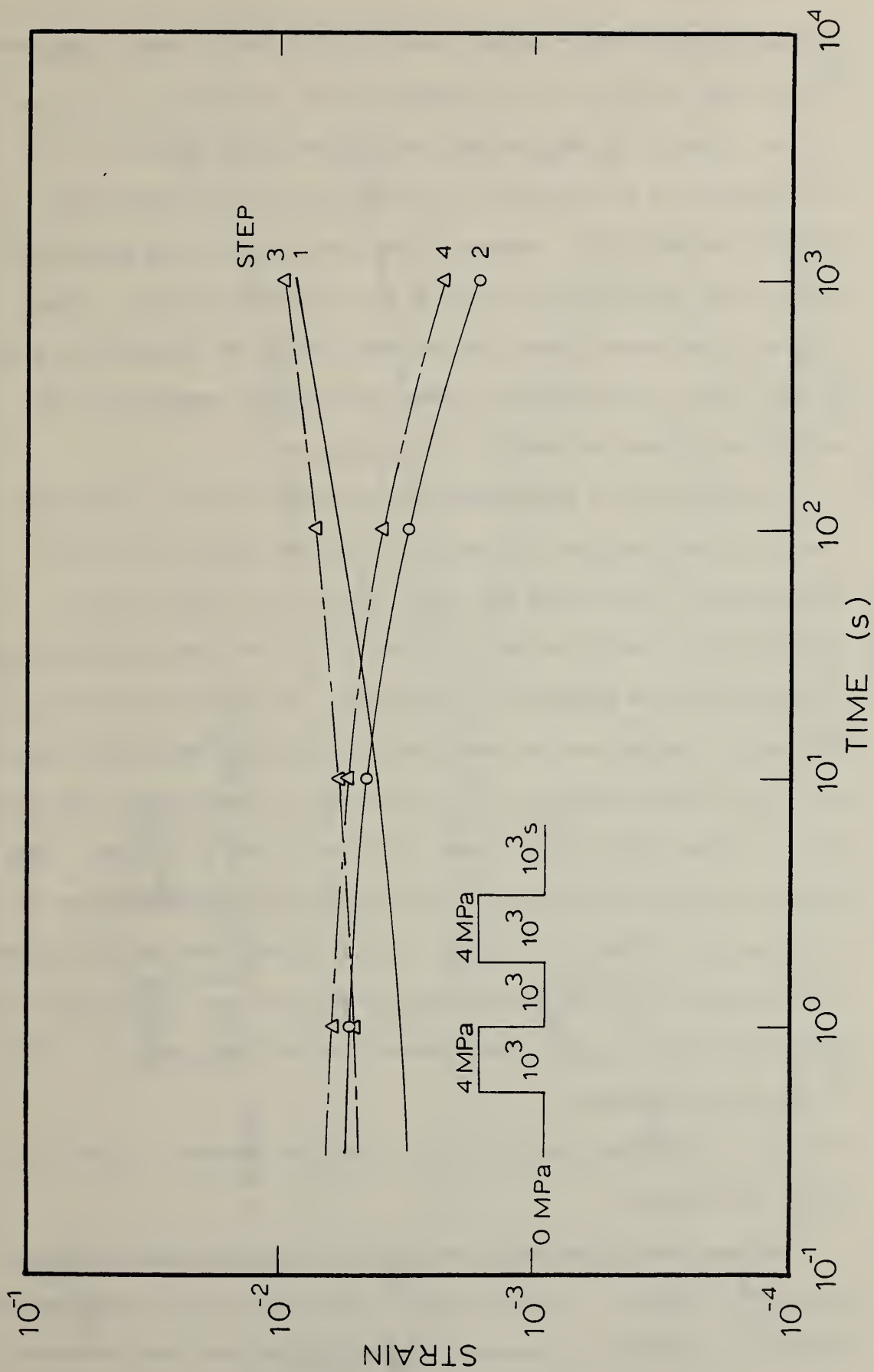


Figure 9 Multistep creep and recovery data for the stress history indicated. The labelling is the same as in Figure 8.

during the third step (second creep step) is significantly larger than during the first step, although at the very long time the two curves appear to be approaching one another asymptotically. For the recovery it is found that the strain during the fourth step (second recovery step) remains larger than that for the second step and as time increases the ratio of the two becomes larger. From similar experiments, where the recovery period was extended to much longer times, the agreement between the observed response and the calculated values was found to be equally good.

A second set of experiments was performed in which the stress histories were similar to those just described except that the extensometer in each case was reset to zero just prior to the application of the third step (at the end of the first recovery step). These results are presented in Figure 10. In this case the creep at the early times is now the same for both the first and third steps, but at the longer times the strain during the second creep step (third step in stress) is somewhat less than that of the first step. This behavior provides an indication that mechanical preconditioning is occurring in the material. Also, it can be seen from Figure 10 that the recovery during the fourth step occurs much more rapidly than during the second step. In fact the recovery is even more rapid than that predicted by equation 1.

### 3.3 Influence of Thermal History on the Creep and Recovery of UHMUPE at Small Deformations

We now compare the creep and recovery behavior of the slowly cooled UH-A (density =  $0.934 \text{ g/cm}^3$ ) to that of the UH-A processed under different conditions. Specimens of the UH-A polymer were prepared either

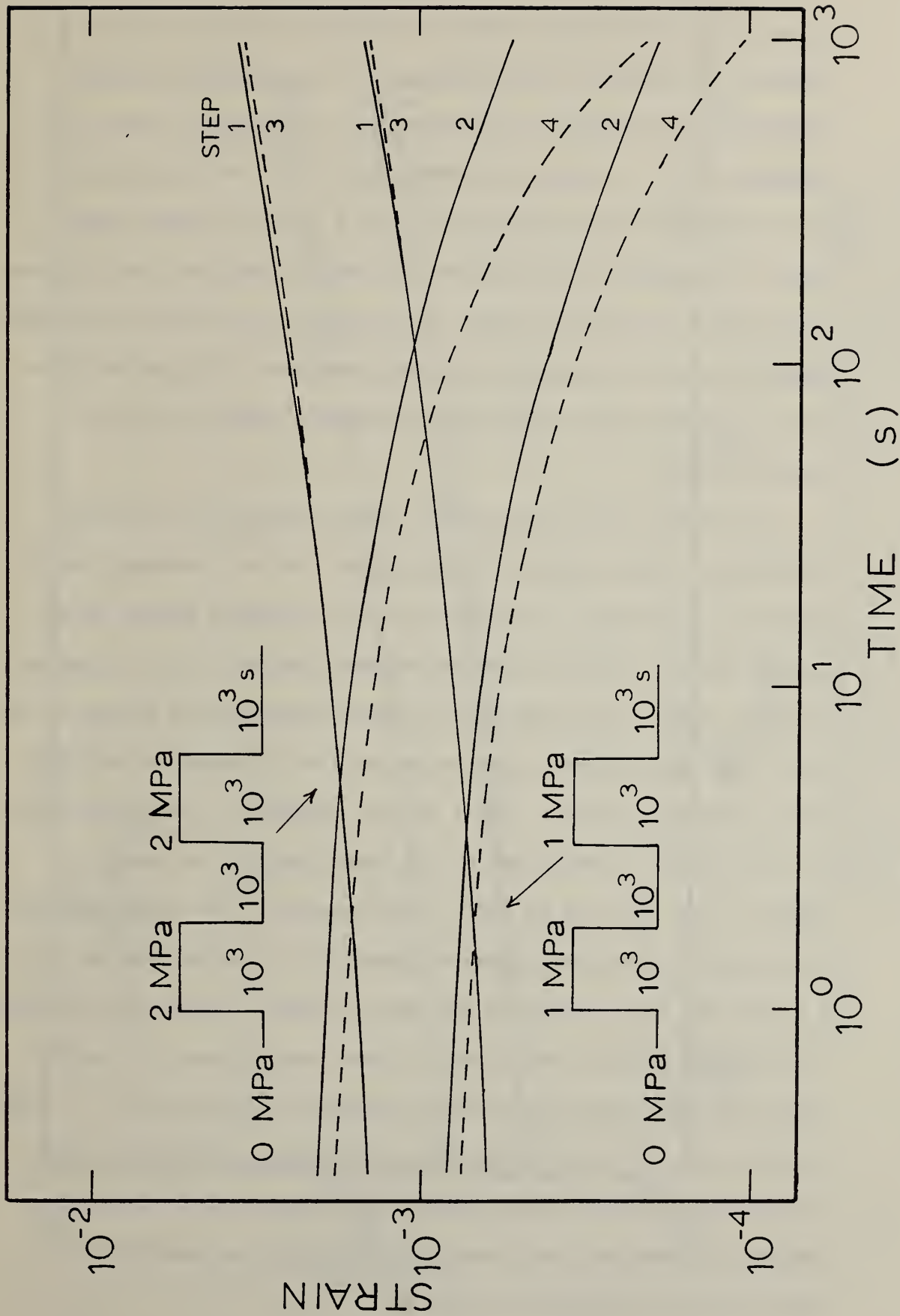


Figure 10 Multistep creep and recovery data for experiments done in which the extensometer was zeroed just prior to the application of the third step. The labelling is the same as in Figure 8.

by quenching the material from the melt into ice water, or by annealing the slowly cooled material at a temperature near the melting point according to procedure (iv) described in Table 1 of reference [2]. The respective densities of the two preparations were  $0.923 \text{ g/cm}^3$  and  $0.940 \text{ g/cm}^3$ . Such a range in density very nearly corresponds to the extremes in density which we have achieved for the UH-A polymer by varying the thermal history during processing. Densities in this range are also representative of those found for pieces cut from unused commercial prosthesis components (see reference [2]).

As was the case in Section 3.1, the deformations were kept sufficiently small so that the experiment can be considered one at constant true stress. In order to keep the maximum strain below about 2 percent, all the experiments were carried out at an applied stress of 4 MPa. For each of the three preparations a series of two step creep and recovery experiments was done in which the applied stress was kept constant (4MPa) and the duration of the creep step,  $t$ , was varied. A comparison of the creep behavior is shown in Figure 11 for the case in which  $t_1=10^3$  seconds. The creep behavior of the slowly cooled and annealed materials is rather similar. At 1 second the creep strain is the same for both, whereas at  $10^3$  seconds the annealed material has actually crept more by about 19 percent. This particular annealing treatment appears to have had only a modest influence on the creep of the UH-A. Quenching, on the other hand, has a significant effect on the creep. For example, at 1 second the quenched polymer has crept nearly twice as much as has either the slowly cooled or annealed polymer.



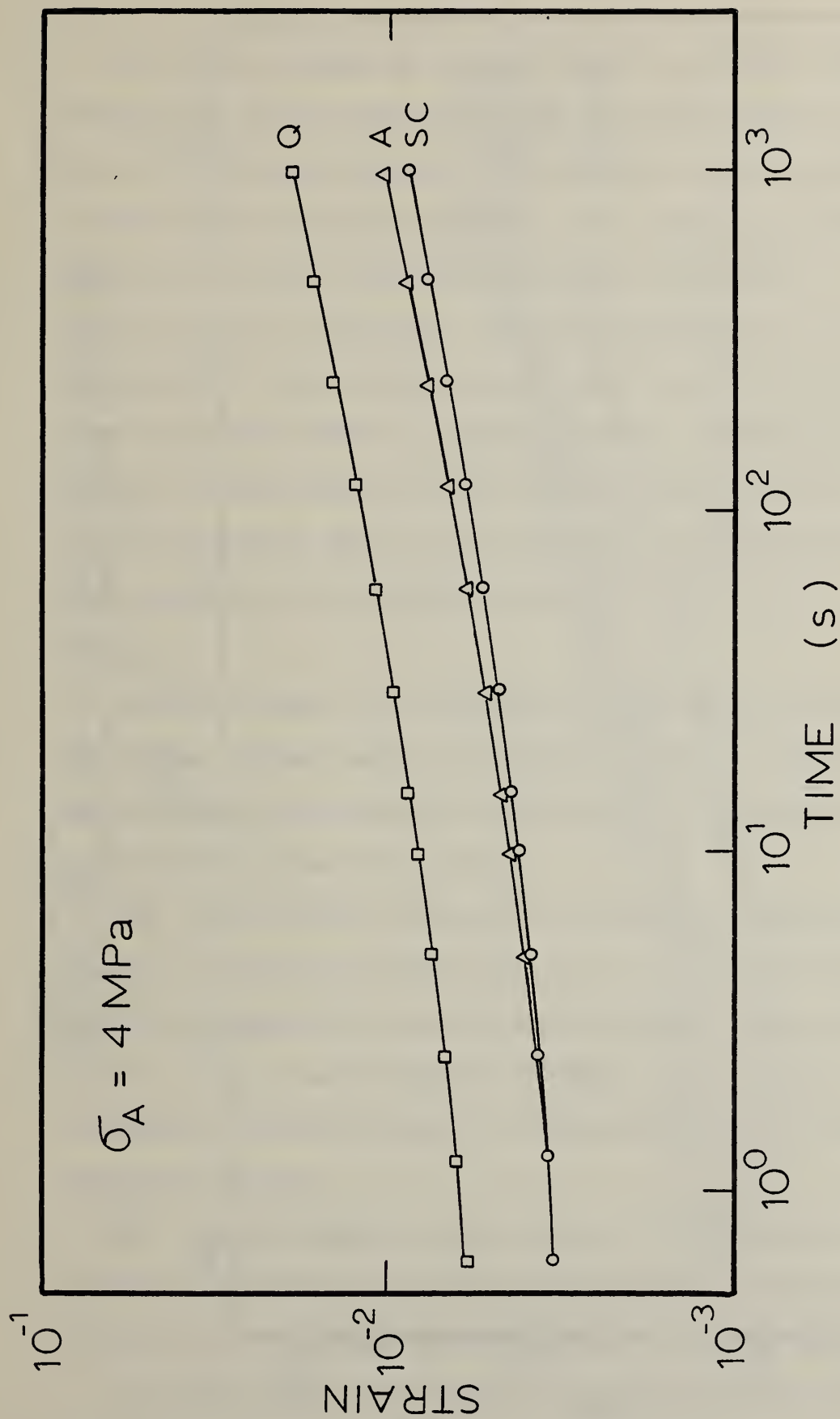


Figure 11 Creep strain versus time (log-log coordinates) for UHMWPE quenched from the melt (Q), slowly cooled from the melt (SC), and slowly cooled from the melt followed by annealing at a temperature near the melting point (A). Applied stress 4MPa.

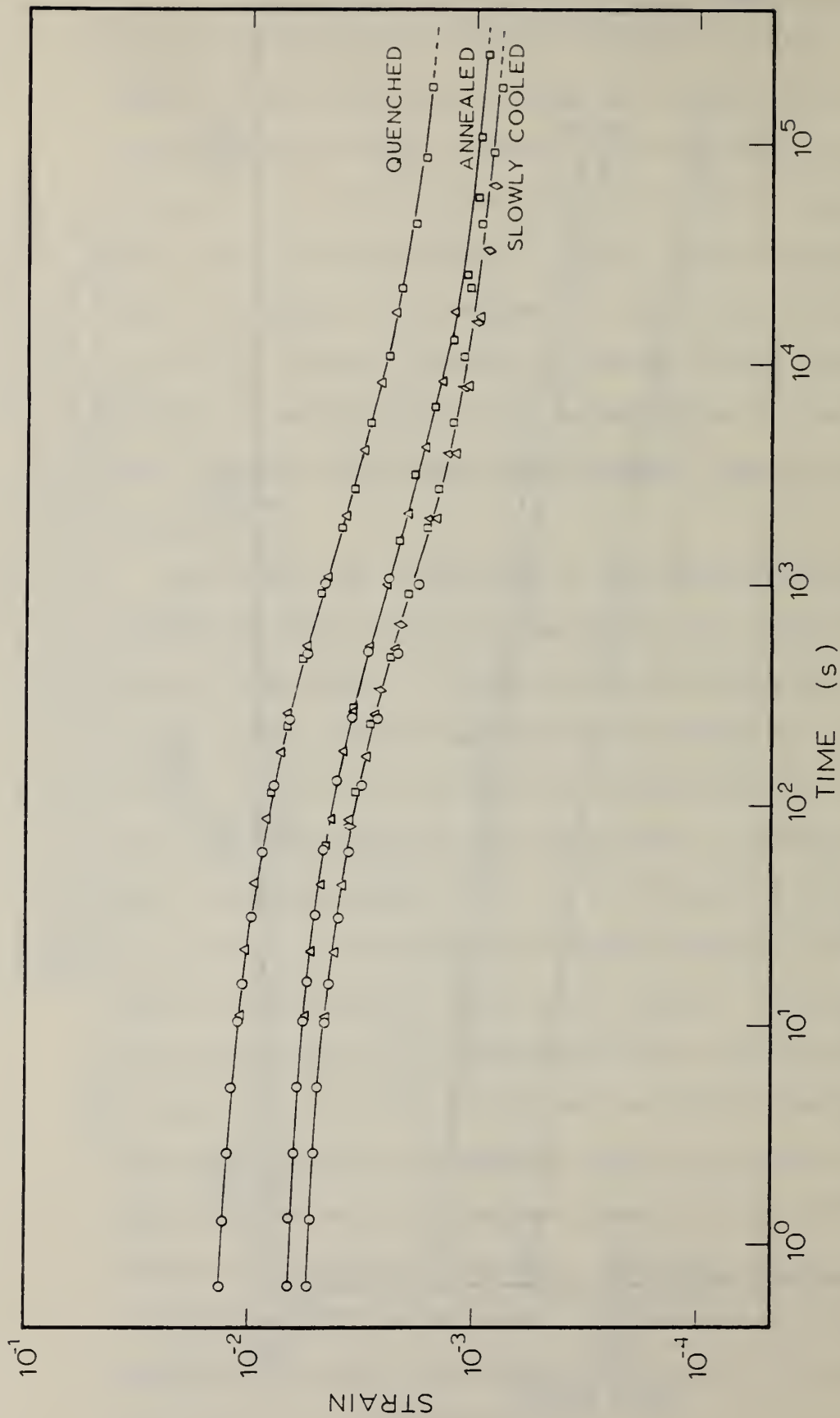


Figure 12 Superposition of recovery data for UHMPE prepared under varied thermal histories. In each case the applied stress during the creep step was 4MPa.



In order to compare the recovery data for the three different preparations, we have followed the same procedures described in Section 3.1 and have superposed onto a master curve the individual recovery curves for each preparations. The results are shown in Figure 12. All three curves show a tendency to plateau to a finite value of strain at long times. It can be observed that at any recovery time,  $t$ , the quenched material has recovered much less than either the slowly cooled or annealed material. The results shown in Figure 12 indicate that for a given recovery time,  $t$ , applied stress,  $\sigma_A$ , and duration of creep,  $t_1$ , the slowly cooled UH-A experienced the least amount of creep and the greatest amount of recovery.

#### 4. Summary

From wide angle x-ray diffraction (WAXD) studies the following qualitative features emerge concerning the effect of strain on the manifestation of polymorphism and the changes in crystallite orientation resulting from uniaxial stretching:

(1) The occurrence of metastable (triclinic) crystallites manifests itself at all strains in the range 0.1 to 1.0. The proportion of triclinic crystallites apparently increases with increasing strain in that range.

(2) From the early stages of deformation the triclinic and orthorhombic crystallites start to orient themselves with respect to the stretching direction.

(3) The distributions in the angle of inclination of the C-Axis in the triclinic and orthorhombic crystallites relative to the stretching direction at a strain of 1.0 are peaked at inclinations of about  $30^\circ$  and  $36^\circ$  respectively.

(4) Upon release from stress, one of the principle changes which occurs when the sample contracts is a substantial decrease in the proportion of triclinic crystallites.

(5) Explanatory experiments clearly indicate that the characterization of the partially reversible uniaxial deformation behavior of UHMWPE will involve not only the quantitative determination of the changes in crystallite orientation, but also quantitative determinations of the relative amounts of the different crystalline forms.

(6) In an attempt to determine the lower limit of deformation at which the occurrence of triclinic crystallites manifests itself, the WAXD of samples stretched to strains as small as 0.05 has been examined. At this junction it can be reported that in samples stretched and held taut at a strain of 0.05 visual evidence of the triclinic form was observed.

Since the ability of UHMWPE to recover after deformation represents an important aspect of durability and lifetime, the creep and recovery behavior of the UHMWPE polymer was examined in the region of small uniaxial deformations. Both two step and multistep experiments were done ( $T=23^{\circ}\text{C}$ ) in which either the duration of creep step was held constant and the applied stress was varied, or the applied stress was held constant and the duration of creep step was varied. In all cases the deformations were kept sufficiently small that the creep portion of the experiment could be considered as one at constant true stress. An important finding from this work is that even after very small deformations the material only partially recovers back toward the initial undeformed state. That is, the strain during recovery tends to plateau to a finite value of strain.

The results of these experiments led us to formulate a new one dimensional constitutive equation which describes plasto-viscoelastic behavior. Using the proposed new equation, and the results from the two step and multistep creep and recovery experiments, we were able to reproduce all of the recovery data to within two percent or better.

The influence of thermal history on the creep and recovery behavior of UHMWPE has also been examined at small deformations. Specimens of the higher molecular weight UHMWPE (UH-A) were prepared by quenching the material from the melt into ice water, by slowly cooling it from the melt, and by annealing the slowly cooled polymer at a temperature near the melting point. The respective densities were  $0.923 \text{ g/cm}^2$ ,  $0.935 \text{ g/cm}^3$ , and  $0.940 \text{ g/cm}^3$ . Under an applied stress of 4MPa the slowly cooled and annealed materials were found to have rather similar creep behavior, the annealed material showing a somewhat more rapid creep subsequent to the initial loading. The quenched material, on the other hand, exhibited nearly twice the amount of creep, under the same applied stress, as that observed for either the slowly cooled or annealed material. Correspondingly, the quenched polymer recovered significantly less than either of the other two preparations. It can be concluded that for a given recovery time, applied stress, and duration of creep, the slowly cooled UH-A exhibited the least amount of creep and greatest amount of recovery.

##### 5. Work Plan for FY 1983

(1) Work started in FY 1982 on the multistep creep and recovery behavior of UHMWPE at small deformations will be extended to include cyclic loading histories ( $\sigma_A = 2.5 - 4\text{MPa}$ ). Histories involving short time loading and unloading over many cycles ( $10^3 - 10^6$ ) will be examined in order to determine whether the creep and recovery can be described by a scheme similar to that developed in sections 3.1 and 3.2.

(2) The influence of temperature on the creep and recovery behavior of UHMWPE at small deformations will be studied in the temperature range from  $23^\circ\text{C}$  to  $50^\circ\text{C}$ .

(3) The effect of irradiation on the creep and recovery behavior of UHMWPE at small deformations will be investigated at 23°C and 37°C for dosages in the range from 1-5 Mrad.

(4) Aspects of the fine structure of undeformed samples which are relevant to their mechanical behavior when subjected to small strains will be examined. In addition when deemed necessary attempts will be made to detect and determine aspects of the fine structural changes resulting from small deformations.



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